Reply to "Remarks on the simulation of Cl electrosorption on Ag(100) reported in Electrochimica Acta 50 (2005) 5518"

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Abstract

We reply to the remarks by Láng and Horányi [Electrochim. Acta Vol. (2006) page] on the meaning of the notion of "electrosorption valency" used in I. Abou Hamad *et al.*, Electrochim. Acta 50 (2005) 5518. It is concluded that, contrary to the assertion of Láng and Horányi, the magnitude of the current in the external circuit upon adsorption of an ion of charge ze with partial charge transfer is indeed given by an electrosorption valency γ such that $|\gamma e| < |ze|$. We believe the conclusion of Láng and Horányi to the contrary is the result of an excessively severe charge-neutrality requirement.

Key words: Electrosorption, Electrosorption valency, Formal partial charge number, Lateral interactions, Surface dipole

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1 Introduction

In their interesting discussion article [1], Láng and Horányi (LH) question the concept of *electrosorption valency* [2,3] as interpreted in our recent paper on Cl electrosorption on Ag(100) [4]. As we understand their argument, its central point is the requirement of charge neutrality in the solution phase and *separately* in a surface layer consisting of the specifically adsorbed ions (traditionally known as the Inner Helmholtz Layer, IHL) and the adjoining part of the metal in the working electrode. These two separate conditions, when applied simultaneously, lead them to the conclusion that the charge transported through the external circuit due to the specific adsorption of an ion of charge ze must be ze, regardless of possible partial discharge of the adsorbate, unless coadsorption of ions of opposite charge takes place.

We argue that this double application of the charge-neutrality requirement overconstrains the problem and leads to an erroneous conclusion. The correct region over which charge neutrality should be applied must include the parts of the solution phase close to the IHL, traditionally known as the Outer Helmholtz layer (OHL) and the diffuse double layer (DDL). See Fig. 1 for definitions of these terms. This polarized region, representing the half-cell of the working electrode, is separated from the rest of the system by fictitious bounding surfaces inside the uniform, macroscopically uncharged bulk media (electrolyte and metal, respectively). This schematic partitioning of the system removes the need to consider the counter electrode explicitly in calculating the charge transport. A completely analogous condition of charge neutrality is independently obeyed at the counter electrode. The current through the working electrode into the external circuit induces a current of opposite sign, but with the same magnitude, through the counter electrode. For instance, if chloride adsorbs at the working electrode, a (partial) negative charge will be released into the external circuit, while a corresponding negative charge will, on average, be injected through the counter electrode. In the present case, this latter charge will most probably transform a corresponding amount of H$^+$ into $\frac{1}{2}$H$_2$, thus maintaining electroneutrality in the entire system.
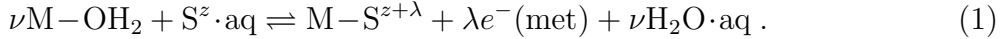
Our conclusion, for which we argue below, is that the expressions for electrosorption valency and adsorbate dipole moment used in Ref. [4] correspond to the approximations of excess supporting electrolyte, as well as to identifying the electrosorption valency with the negative of the partial charge-transfer coefficient. While not exact, these are reasonable approximations, supported *a posteriori* by the good agreement between the numerical results for our model system and the experimental adsorption isotherms. In the process we reconfirm Vetter and Schultze's relation between the electrosorption valency and the current in the external circuit [3].

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Details of our arguments, including the approximations used in Ref. [4] (and also in Ref. [5]), are given below. In Sec. 2 we discuss the definition of the electrosorption valency; in Sec. 3 we discuss its relation to the current in the external circuit; and in Sec. 4 we obtain its relation to the surface dipole moment. Our conclusions are summarized in Sec. 5.

2 Electrosorption Valency

The electrosorption valency was thermodynamically formalized by Vetter and Schultze [2,3] to account for the current in the external circuit during electrosorption with partial charge transfer [6]. Abbreviated derivations have been presented later (see, e.g., Ch. 18 of Ref. [7]), but we believe the most detailed treatment is given in Refs. [2,3], as supplemented by Refs. [8,9,10]. Results of these early papers were recently summarized by Schultze and Rolle [11,12].

Vetter and Schultze consider an electrosorption reaction for an ion of valence z with the possible charge transfer of a noninteger number λ of electrons, described by the equation [2,3,8,9,10]

$$\nu \mathrm{M-OH_2} + \mathrm{S}^z \cdot \mathrm{aq} \rightleftharpoons \mathrm{M-S}^{z+\lambda} + \lambda e^-(\mathrm{met}) + \nu \mathrm{H_2O} \cdot \mathrm{aq} \ . \tag{1}$$

To avoid extrathermodynamic complications arising from considering the microscopic structure of the DDL [13], we here restrict ourselves to the case of excess supporting electrolyte, so that the potential at the OHL, ϕ_{OHL}, is the same as that in the bulk electrolyte, ϕ_{e}, [2,3,9], which we can define equal to zero without loss of generality. See Fig. 1. This is indeed the condition corresponding to the experiments reported in Refs. [4,5]. The electrode potential is then $E = \phi_{\mathrm{met}} + \mathrm{cst.}$, where ϕ_{met} is the potential of the metal. Thus, in the case of excess supporting electrolyte, differentiation with respect to E is the same as with respect to $(\phi_{\mathrm{met}} - \phi_{\mathrm{OHL}})$. The excess of supporting electrolyte also reduces the concentration of adsorbate ions S^z in the DDL, while a relatively low concentration of adsorbate ions relative to the solvent reduces their concentration in the OHL relative to the IHL. In this approximation we can therefore replace the total surface excess of adsorbate ions, Γ_{S}, by the surface coverage θ of the specifically adsorbed, partially discharged species $\mathrm{S}^{z+\lambda}$ in the IHL [2]. The coverage is defined as the number of specifically adsorbed ions per adsorption site on the surface. In what follows, we shall use θ as an approximation for the more general Γ_{S}.

In Ref. [2], the electrosorption valency is defined as

$$\gamma = \left(\frac{\partial \mu_{\mathrm{S}}}{\partial E} \right)_\theta \ , \tag{2}$$

where μ_S is the *chemical* potential of S^z in the bulk solution. From this and a general adsorption isotherm corresponding to the reaction equation (1), they obtain the relation

$$\gamma = \gamma_{PZC} - \frac{1}{e} \int_{E_{PZC}}^{E} \left(\frac{\partial C_D}{\partial \theta} \right)_E \mathrm{d}E' , \tag{3}$$

where e is the elementary charge unit and C_D is the capacitance of the compact double layer (metal vs. IHL). The subscript PZC refers to the Potential of Zero Charge. The value of γ at the PZC is

$$\gamma_{PZC} = gz - \lambda(1 - g) + \kappa_{ad} - \nu\kappa_w . \tag{4}$$

Here, κ_{ad} and κ_w refer to the effects of the dipole moments of the adsorbate and water, respectively, and can usually be neglected for inorganic, aqueous electrolytes. The factor $g = (\phi_{IHL} - \phi_{OHL})/(\phi_{met} - \phi_{OHL})$ is the ratio of the potential difference between the adsorbate and the OHL to that between the metal and the OHL and is frequently of the order of 0.2. A simple interpretation of the schematic Fig. 1 with a near-linear potential profile would lead to the traditional interpretation of g as a purely geometric factor. For more realistic microscopic models that lead to a nonlinear potential profile, such as illustrated in Fig. 1, the connection of g to the geometry of the interface region is less clear.

Equations (3) and (4) reveal two important approximations in our Refs. [4,5]. The first is that the integral in Eq. (3) is approximated by a linear function in the coverage θ. This is reasonable since any changes in γ with E are likely to be largely due to the increased crowding on the surface.

The second approximation, which is expressed in Sec. 2.2 of our Ref. [4] (and also quoted verbatim in the fifth paragraph of LH [1]), is that we take $g = 0$. This leads to Lorentz' approximation $\gamma_{PZC} = -\lambda$ [6] and corresponds to the situation that the full potential drop happens between the bulk metal and the IHL. A somewhat better approximation is probably the minimum value for water, $g_{min} \approx 0.16$, obtained by Schultze and Koppitz [10].

3   Surface Charge and Potentiostatic Current

The crucial problem of the interpretation of γ in terms of the current in the external circuit is treated by Vetter and Schultze in Ref. [3]. The central point is that even a partial discharge corresponding to $\lambda \neq 0$ merely corresponds to a *redistribution of charge in the interface region*. Therefore, all currents in the

circuit are *capacitive*, corresponding to changes in the excess charge density on the metal, q_{met}, and the corresponding quantity on the electrolyte side, q_{e}. (By the requirement of charge neutrality, $q_{\mathrm{e}} = -q_{\mathrm{met}}$.) Considering q_{met} as a function of θ and E, one thus gets the current density

$$i = \frac{\mathrm{d}q_{\mathrm{met}}}{\mathrm{d}t} = \left(\frac{\partial q_{\mathrm{met}}}{\partial \theta}\right)_E \frac{\mathrm{d}\theta}{\mathrm{d}t} + \left(\frac{\partial q_{\mathrm{met}}}{\partial E}\right)_\theta \frac{\mathrm{d}E}{\mathrm{d}t} \ . \tag{5}$$

From the electrocapillary equation for the compact double layer (i.e., the full differential of the surface free energy density or "surface tension" σ),

$$-\,\mathrm{d}\sigma = (z_{\mathrm{met}}\Gamma_{\mathrm{met}} - \Gamma_{e^-} + \lambda\theta)e\,\mathrm{d}E + \theta\mathrm{d}\mu_{\mathrm{S}} + \sum_j \Gamma_j \mathrm{d}\mu_j \ , \tag{6}$$

they obtain

$$q_{\mathrm{met}} \equiv \left(\frac{\partial \sigma}{\partial E}\right)_{\mu_{\mathrm{S}},\mu_j} = (z_{\mathrm{met}}\Gamma_{\mathrm{met}} - \Gamma_{e^-} + \lambda\theta)e \ , \tag{7}$$

where z_{met}, Γ_{met}, and Γ_{e^-} refer to the ions and conduction electrons of the electrode. The current density *at constant potential*, i_{pot}, is thus obtained from Eq. (5) by setting $\mathrm{d}E/\mathrm{d}t = 0$. The necessary relation to γ as defined in Eq. (2) is found by writing

$$\left(\frac{\partial q_{\mathrm{met}}}{\partial \theta}\right)_E = \left(\frac{\partial q_{\mathrm{met}}}{\partial \mu_{\mathrm{S}}}\right)_E \left(\frac{\partial \mu_{\mathrm{S}}}{\partial \theta}\right)_E \tag{8}$$

and using the Maxwell relation obtained from the electrocapillary equation,

$$\left(\frac{\partial q_{\mathrm{met}}}{\partial \mu_{\mathrm{S}}}\right)_E = \left(\frac{\partial \theta}{\partial E}\right)_{\mu_{\mathrm{S}}} \ , \tag{9}$$

together with the standard equality for any three quantities related by a single equation,

$$\left(\frac{\partial \theta}{\partial E}\right)_{\mu_{\mathrm{S}}} \left(\frac{\partial E}{\partial \mu_{\mathrm{S}}}\right)_\theta \left(\frac{\partial \mu_{\mathrm{S}}}{\partial \theta}\right)_E = -1 \ . \tag{10}$$

Thus,

$$i_{\mathrm{pot}} = \left(\frac{\partial q_{\mathrm{met}}}{\partial \theta}\right)_E \frac{\mathrm{d}\theta}{\mathrm{d}t} = -\gamma e \frac{\mathrm{d}\theta}{\mathrm{d}t} \ . \tag{11}$$

To appreciate this derivation it is important to realize that the current at constant potential is not a simple quantity. As pointed out by Schmickler [14], conceptually it involves two steps: first the adsorption of the ion and corresponding buildup of the image charge, *which changes the potential*, followed by readjustment of the charges to bring the potential back to its original value. Without a detailed, microscopic model, these semimacroscopic, thermodynamic results cannot tell us in detail how the charges are distributed in the interface region. This is a major limitation of the concept of electrosorption valency.

The applicability of the results summarized above to reversible electrodes (as opposed to perfectly polarizable ones) was questioned by Frumkin, Damaskin, and Petrii in Ref. [13]. In response, Vetter and Schultze explicitly established the validity of their results for reversible electrodes in Ref. [9].

4 Surface Dipole Moment

While the quantities discussed in Sec. 3 are purely thermodynamic quantities (in the case of excess supporting electrolyte), a microscopic theory of the interface structure is necessary to estimate the dipole moment associated with adsorption of an ion [14,15,16]. Generally, the dipole moment of a (one-dimensional) charge distribution $q(x)$ is defined as

$$p = \int_{x_1}^{x_2} x \, q(x) \, \mathrm{d}x \; .$$

(12)

The result is independent of the coordinate system if the integration limits are chosen such that charge neutrality is obeyed over $[x_1, x_2]$: $\int_{x_1}^{x_2} q(x) \, \mathrm{d}x = 0$ [17]. The charge distribution produces a potential difference, $\phi_2 - \phi_1 = p/\epsilon$, where ϵ is the dielectric constant of the medium. The details depend on the microscopic model.

The approximation used in Ref. [4] is the commonly used one [18,19], due to Bange et al. [20] and Schmickler [7,14],

$$p = \frac{ze\epsilon}{C_\mathrm{H}} \left(1 - \frac{\gamma}{z} \right) \; ,$$

(13)

where C_H is the Helmholtz capacity. This result is derived under the condition of charge neutrality (but not necessarily vanishing dipole moment) over the DDL. It can be obtained simply within the picture illustrated in Fig. 1 as follows. The dipole moment is related to the potential drop from the metal

to the layer of specifically adsorbed ions as $p = \epsilon(\phi_{\text{met}} - \phi_{\text{IHL}}) = \epsilon(1-g)E$. Assuming the field dependence of γ in Eq. (3) can be included in g and λ, and ignoring the polarization terms κ when solving Eq. (4) for $(1-g)$, we obtain

$$p = \frac{z\epsilon E}{z + \lambda}\left(1 - \frac{\gamma}{z}\right) . \tag{14}$$

By setting $C_{\text{H}} = e(z+\lambda)/E$, we get Eq. (13), which can be rewritten in terms of $(1-g)$ and the partial charge-transfer coefficient λ as

$$p = \frac{ze\epsilon}{C_{\text{H}}}(1-g)\left(1 + \frac{\lambda}{z}\right) . \tag{15}$$

The prefactor $ze\epsilon/C_{\text{H}}$ can be viewed as an effective *dipole distance*. However, due to screening by both the liquid and the electron gas of the metal, this distance is generally much smaller than the ionic radius of the adsorbate [14,15]. Equation (15) with $g = 0$ was the one used in Ref. [4] for the dipole moment, and therefore for the lateral adsorbate interactions.

An alternative approach is to consider the surface dipole moment as the basic, physical quantity, and γ as a derived quantity linked to p by Eq. (13) under assumption of the geometric model described in Fig. 1.

5 Conclusion

In this discussion paper we have summarized arguments showing that the electrosorption valency γ as defined by Vetter and Schultze [2] gives the correct result for the current in the external circuit due to adsorption of an ion of charge ze, Eq. (11) [3], as well as the relation between γ and the charge-transfer coefficient λ, Eq. (4) [2]. These results show that there is no need for coadsorption with an oppositely charged ion to reduce the current per adsorbate particle from ze, to γe. We note that the derivation of these results requires charge neutrality over the whole interface region, as indicated in Fig. 1, not separately over the electrolyte and the compact double layer, as we understand the argument of LH to imply. We believe the reason for their conclusion that partial charge transfer cannot change the current is a result of their overly strict charge-neutrality requirement.

Beyond these general results, we have shown that the approximations used in Refs. [4,5] are excess supporting electrolyte and vanishing of the factor g. While certainly not exact, these assumptions are reasonable for the systems studied and give very good agreement between the computer simulations of the lattice-gas model and the experimental adsorption isotherms.

Finally we note that the arguments given here are based on classical thermodynamics with no specific assumptions on the microscopic structure of the interface region, beyond the charge neutrality. In order to obtain explicit results for microscopic parameters without fitting to experiments, one would need quantum-statistical-mechanical calculations that are still beyond our computational capacity. Only such future calculations have the potential to determine explicitly such quantities as the surface dipole moment and the spatial distribution of charge and dipole moments in the whole interfacial region.

Acknowledgments

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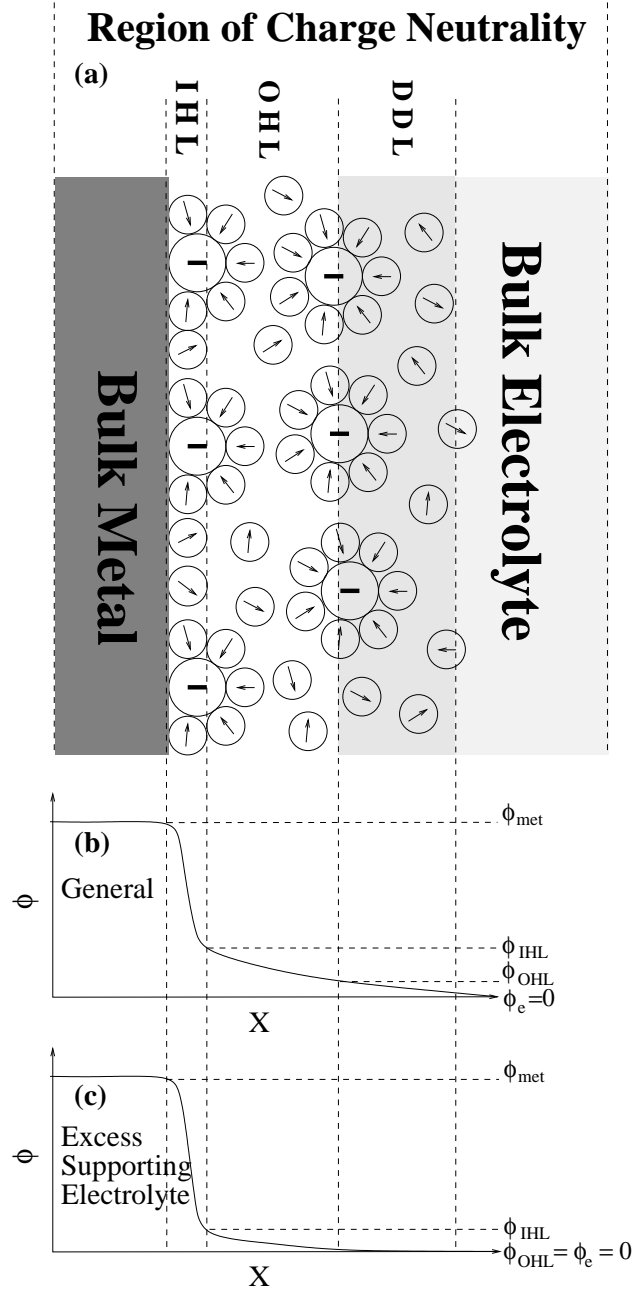[20] K. Bange, B. Straehler, J. K. Sass, R. Parsons, J. Electroanal. Chem. 229 (1987) 87–98.

Fig. 1. Schematic picture of the interface region at the working electrode **(a)**, the electrostatic potential ϕ as a function of distance x perpendicular to the surface in the general case **(b)** and in the case of excess supporting electrolyte **(c)**. Here, IHL stands for the inner Helmholtz layer, OHL for the outer Helmholtz layer, and DDL for the diffuse double layer. Large circles with a minus sign represent the adsorbate ions, and small circles with an arrow indicating a dipole moment represent water molecules. After Ref. [2].